On the Misuse of Le Chatelier’s Principle for the Prediction of the Temperature Dependence of the Solubility of Salts

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In the course of their discussions of Le Chatelier’s principle, many textbooks direct attention to the effect of three forms of stress on a system at equilibrium: (1) the addition or removal of an excess reactant or product, (2) changes in the pressure of a gaseous system, and (3) changes in the temperature of the system. The first two forms of stress lead to a shift in the position of the equilibrium, without affecting the magnitude of the equilibrium constant. Changes in the temperature of the system, however, lead to a change in the magnitude of the equilibrium constant as well.

Le Chatelier’s principle, as it is commonly expressed, suggests that a stress applied to a system at equilibrium will lead to a shift in the position of the equilibrium which minimizes the effect of that stress. It is therefore often argued that the magnitude of the equilibrium constant for endothermic reactions, in which heat is absorbed from the surroundings,

\[ \text{reactants + heat} \rightarrow \text{products} \quad (\Delta H = +) \]

will increase with increasing temperature. Conversely, exothermic reactions, in which heat is liberated,

\[ \text{reactants} \rightarrow \text{products + heat} \quad (\Delta H = -) \]

are characterized by a decrease in the equilibrium constant with increasing temperature.

Numerous authors assume that this concept can be applied to saturated solutions in which a dynamic equilibrium exists between a solid solute and its solution. They suggest that endothermic reactions of the type

\[ \text{solute + solvent + heat} \rightarrow \text{solution} \quad (\Delta H = +) \]

will be reflected by an increase in solubility with increasing temperature. Exothermic reactions

\[ \text{solute + solvent} \rightarrow \text{solution + heat} \quad (\Delta H = -) \]

would then be reflected by a decreased solubility with increasing temperature. Among the examples which are commonly invoked to support this argument are Na₂SO₄·10 H₂O, NaCl and KNO₃, for which the enthalpy of solution is positive, and Na₂SO₄, Ca(OH)₂ and NaI for which the enthalpy of solution is negative.¹

Unfortunately, we run into several points of confusion when we attempt to apply this hypothesis to the prediction of the temperature dependence of the solubility of inorganic salts. For example, the enthalpies of solution of NaCl and NaI have different signs, as noted above, and yet both salts exhibit an increased solubility with increasing temperature. Furthermore, we know from experience that NaOH evolves heat when dissolved in water (\(\Delta H = -\)), suggesting that the solubility of NaOH in water should decrease with increasing temperature, and yet the solubility of NaOH increases by roughly a factor of ten between 0°C and 100°C. In fact, of the 31 salts of sodium for which data are available, 14 have negative enthalpies of solution, and yet only one, Na₂SO₄, shows a decreased solubility with increasing temperature.

Careful examination of the available data leads to the conclusion that there is no obvious relationship between the sign of the enthalpy of solution tabulated in the various handbooks and the change in the solubility of inorganic salts with temperature. Some appreciation for the magnitude of this problem can be obtained by examining the enthalpy of solution data for alkali metal and alkaline earth halides given in the table. It is worth noting that each and every one of these salts shows an increased solubility with increasing temperature in the range from 0°C to 100°C, regardless of the sign or magnitude of the enthalpy of solution.

Discussion

To understand why this seemingly simple application of a universally accepted principle might fail we must first understand: (1) why Le Chatelier’s principle can be applied to the temperature dependence of the equilibrium constant, (2) why small changes in the nature of a salt can lead to changes in both the magnitude and sign of the enthalpy of solution, and (3) why the term enthalpy of solution is intrinsically vague.

Starting from the definition of standard state changes in the Gibbs’s free energy of a system,

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

and the relationship between \(\Delta G^\circ\) and the equilibrium constant, \(K\),

\[ \Delta G^\circ = -RT \ln K \]

we can derive the following equation:

\[ \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

As we can see, the contribution to the equilibrium constant from entropy is temperature independent. Thus, differentiation of \(\ln K\) with respect to temperature leads inevitably to the conclusion that the magnitude and sign of \(\Delta H^\circ\) determine the effect of temperature on the equilibrium constant.

\[ \frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \]

\[ \frac{d\ln K}{dT} = -\frac{\Delta H^\circ}{R} \]

What factors control the sign and magnitude of the enthalpy of solution of a substance? We might start by considering what happens when a solid solute dissolves in a liquid solvent. This process can be formally divided into two thermodynamic steps,

\[ \text{solid solute} \rightarrow \text{liquid solute} \]

\[ \text{liquid solute + solvent} \rightarrow \text{solution} \]

such that the enthalpy of solution (\(\Delta H_{\text{soln}}\)) is the sum of \(\Delta H_1\) and \(\Delta H_2\). In this formalism, \(\Delta H_1\) corresponds to the enthalpy of fusion of the solute, or the energy associated with the melting of the solid. \(\Delta H_2\) is the enthalpy of mixing, the heat liberated or absorbed when the solute and solvent are mixed. An ideal solution, by definition, results from the athermal

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¹ There is some confusion concerning the sign convention for enthalpies of solution. Data are frequently tabulated using the rather unusual convention that positive enthalpies of solution are assigned to salts which liberate energy when dissolved in water, i.e., exothermic dissolution reactions. We have adopted the convention that exothermic processes will be assigned negative enthalpies, and therefore the enthalpy of solution for NaOH at infinite dilution is ~10.637 kcal/mole.


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Integral Molar Enthalpies of Solution at Infinite Dilution for Alkali and Alkaline Earth Halides \(^{a,b}\)

<table>
<thead>
<tr>
<th></th>
<th>X:</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
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</thead>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.059</td>
<td>-8.818</td>
<td>-11.717</td>
<td></td>
<td>-15.1 Kcal/mole</td>
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<td>0.914</td>
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<td>-1.81</td>
<td></td>
</tr>
<tr>
<td>K</td>
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<td>4.85</td>
<td>4.93</td>
<td></td>
</tr>
<tr>
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<td>4.28</td>
<td>5.285</td>
<td>6.50*</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
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<td>6.24</td>
<td>7.46</td>
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</tr>
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<td>-43.3</td>
<td>-49.8</td>
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<tr>
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<td>-2.98</td>
<td>-5.61</td>
<td>-10.3*</td>
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</tbody>
</table>


\(^{b}\) Data determined at 25°C unless specified by an *.

The integral molar enthalpy of solution, \(\Delta H_{\text{sol}}\), may be defined as the total heat liberated or absorbed when one mole of solute is dissolved in \(n_b\) moles of solvent. \(\Delta H_{\text{sol}}\) may therefore be measured at any concentration. The most common measurement, however, is the integral molar enthalpy of solution at infinite dilution, \(\Delta H_{\text{sol}}^{\text{d}}\), or the total heat associated with the dissolution of one mole of solute in an infinite amount of solvent. The “heat of solution” tabulated in various reference manuals is actually the integral molar enthalpy of solution at infinite dilution. Unfortunately, there is no intrinsic reason why the sign of \(\Delta H_{\text{sol}}^{\text{d}}\) should be related to the temperature dependence of the solubility of a solute.

The temperature dependence of solubility should be related to the differential molar enthalpy of solution, \(\Delta H_{\text{sol}}^{\text{d}}\), the intercept on the vertical axis in the figure of a tangent at any point on the curve (2). Furthermore, the only value of \(\Delta H_{\text{sol}}^{\text{d}}\) of immediate interest is the differential molar enthalpy of solution at saturation, \(\Delta H_{\text{sol}}^{\text{d, last}}\), since the only question of significance is whether heat is evolved or absorbed as the system approaches equilibrium. Any success at the application of tabulated heat of solution data for simple covalent substances dissolved in weakly interacting solvents must be attributed to the monotonous consistency of the sign of \(\Delta H_{\text{sol}}^{\text{d}}\), and therefore perhaps \(\Delta H_{\text{sol}}^{\text{d, last}}\) for these systems.

For ionic substances dissolved in aqueous solution, where the sign of both \(\Delta H_{\text{sol}}^{\text{d}}\) and \(\Delta H_{\text{sol}}^{\text{d, last}}\) is less regular, the naive application of \(\Delta H_{\text{sol}}^{\text{d, last}}\) data leads to purely random results, as we suggested above. Mazo and Bernhard (3) have noted previously that whereas the integral molar enthalpy of solution at infinite dilution, \(\Delta H_{\text{sol}}^{\text{d}}\), for sodium acetate is \(-4.140\) kcal/mole, the differential molar enthalpy of solution at saturation, \(\Delta H_{\text{sol}}^{\text{d, last}}\), is zero or slightly positive, thereby explaining to their satisfaction the increased solubility of sodium acetate with increasing temperature. There are, however, only a very limited number of compounds for which sufficient data are available to estimate \(\Delta H_{\text{sol}}^{\text{d, last}}\), and this concept is therefore of questionable utility.

We have determined values of \(\Delta H_{\text{sol}}^{\text{d, last}}\) by graphical extrapolation for approximately 20 salts of the alkali and alkaline earth metals (4). For most of the alkali metal halides the extrapolated value of \(\Delta H_{\text{sol}}^{\text{d, last}}\) is effectively zero, or slightly positive, in accord with the observed increase in solubility with increasing temperature. However, the data are not sufficiently well-characterized to allow prediction of the temperature...
dependence of solubility with any degree of precision. Furthermore, while the value of ΔH_{sol}^{d} for NaOH becomes progressively less negative as saturation is approached, the extrapolated value of ΔH_{sol}^{d, last} appears to be on the order of −2 kcal/mole, and it appears that ΔH_{sol}^{d} for NaBr becomes increasingly more negative as saturation is approached. Neither result is in agreement with the observed temperature dependence of the solubility of these salts. Unfortunately, the situation becomes considerably worse when we apply this analysis to salts of the alkaline earth metals. The extrapolated values of ΔH_{sol}^{d, last} for Mg(NO₃)₂, MgCl₂ and MgBr₂ range from −20 to −40 kcal/mole. Yet in each case solubility increases with increasing temperature.

It is tempting to offer an explanation for this anomalous behavior, and a number of factors may be involved. (1) Our treatment of equilibria in saturated solutions is notoriously naive. We assume that all of the solute (M, Xₙ) dissolved in aqueous solution can be accounted for on the basis of M^{n+}(aq) and X⁻(aq) ions, neglecting any association between ions or M, X fragments in solution (5). (2) The equilibrium constant of interest represents the ratio of activities not concentrations, and it is well documented that activities in saturated solutions of salts are far from well-behaved. (3) The nature of the substance undergoing dissolution changes with temperature due to changes in the extent of hydration, leading to well-documented changes in the magnitude of both the enthalpies of solution and the solubilities. (4) There are certain types of systems which do not obey Le Chatelier’s principle under all conditions (6). Open systems, in particular, are subject to violations of this principle (7).

Conclusion

It would appear that application of Le Chatelier’s principle and enthalpy of solution data to the prediction of the temperature dependence of the solubility of salts can lead to wrong answers, even under the most stringent conditions. In the hands of the novice, purely random results are obtained.

Given the desire to generalize the temperature dependence of the solubilities of inorganic salts in aqueous solution, we might suggest that the solubility generally increases with increasing temperature. Over 94% of the salts for which data are tabulated in the Handbook of Chemistry and Physics satisfy this generalization. Purists might then note that over two-thirds of the exceptions to this statement are salts of the following oxyanions: SO₄^{2−}, SeO₃^{2−}, SO₃^{2−}, AsO₃^{3−} and PO₄^{3−}.

Acknowledgment

It is indeed a pleasure to recognize the contribution of J. Dudley Herron and students in the Chemistry Teachers Workshop at Purdue University who initially raised a “simple” question in thermodynamics.

Literature Cited
